



Short communication

Phosphorus derivatives as electrolyte additives for lithium-ion battery: The removal of O₂ generated from lithium-rich layered oxide cathode

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HIGHLIGHTS

- Phosphorus derivatives can absorb O₂ generated from Li-rich layered oxide cathode.
- The cell internal pressure at the end of charging can be significantly reduced.
- Phosphorus derivatives also improve the cycle life when used as additives.

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ABSTRACT

Direct internal pressure measurements of the cylindrical Li-ion cells with a mixture of LiCoO₂ and Li_{1.167}Ni_{0.233}Co_{0.1}Mn_{0.467}Mo_{0.033}O₂ (a solid solution between 0.4 Li₂Mn_{0.8}Ni_{0.1}Mo_{0.1}O₃ and 0.6 LiNi_{0.4}Co_{0.2}Mn_{0.4}O₂) as cathode and graphite as anode have been performed during cell charging. Cell internal pressure at the end of charging is greatly reduced from 2.85 to 0.84–1.84 bar by adding a small amount of phosphorus derivatives such as triphenyl phosphine (TPP), ethyl diphenylphosphinite (EDP), and triethyl phosphite (TEP) into a carbonate-based electrolyte. The phosphorus derivatives are supposed to react with O₂ generated from the decomposition of the Li₂MnO₃ component. The chemical states of additive molecules before and after the charging process have been characterized with a nuclear magnetic resonance (NMR) spectroscopy and gas chromatography–mass spectrometry (GC–MS). It has also been shown that those additives improve the cycle life when applied in coin full cells.

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1. Introduction

Li-ion batteries rapidly become essential for powering today's mobile electronic devices as they exhibit high energy density and long cycle life compared with other rechargeable systems [1]. While the research of electrode materials for Li-ion battery is usually covering how to store more energy repeatedly, the electrolyte research is typically restricted to overcoming its own issues such as enlarging electrochemical window, forming a better SEI layer, increasing ionic conductivity, and improving safety [2]. However, the importance of electrolyte is growing and more functions of electrolyte are demanded for the practical use of advanced Li-ion batteries especially to employ new electrode

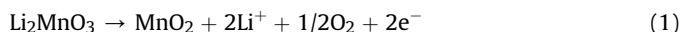
materials. We show in this study an example of electrolyte design circumventing a safety issue of the cell by scavenging the oxygen gas evolved from cathode material.

A major challenge of Li-ion battery research is to develop systems with even higher energy and power densities, especially satisfying the requirements of electric vehicles or new multifunctional portable electronics. In this regard, Li-rich Mn-based layered oxide cathode materials – denoted below as overlithiated layered oxide (OLO) for simplicity – with a formula of Li[Li_xMn_yM_z]O₂, where M represents one or more transition metal elements, are considered to be promising for advanced Li-ion batteries due to their high rechargeable capacity (>200 mAh g^{−1}), good thermal stability, and low cost compared with widely used LiCoO₂ [3–8].

Despite those advantages, the charging of OLO cathode over 4.5 V vs. Li/Li⁺ causes irreversible decomposition of its surface positioned Li₂MnO₃ component, generating O₂ gas. The reaction can be represented as in Equation (1).

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Several research groups showed direct evidence of O_2 generation using *in situ* differential electrochemical mass spectrometry (DEMS) [9–11] and *ex situ* gas chromatography (GC) [12]. Those reports focused on proving the generation of O_2 gas, and efforts to solve the issue in practical battery systems are not yet made. Since the increase in internal pressure might activate the ventilation system of the cell or cause safety problems, the pressure of oxygen inside the cell should be kept as low as possible. Our previous results showed the surface coating of OLO powder or electrode with VO_x , Al_2O_3 , or AlPO_4 mitigated the evolution of oxygen to a significant extent [13,14]. However, considering the cell might experience elevated temperatures while being used by customers, the possibility of potential oxygen evolution still remains since part of Li_2MnO_3 phase is not activated in the first charging process.

In this study, we demonstrated the reduction of internal pressure to the level of one third by using phosphorus derivatives as electrolyte additives, which can react with O_2 forming stable compounds. It is noted that phosphorus derivatives have occasionally been used as flame retardant for Li-ion batteries [15–18]. For the direct measurement of cell internal pressure, we used cylindrical Li-ion cells of 18650 size linked to a pressure sensor with a blend of LiCoO_2 and OLO as cathode and a graphite as anode. Also, we investigated the influence of such additives on the cycle life of coin full cells.

2. Experimental

The overlithiated layered oxide (OLO) powder was synthesized as described in a previous report [19]. The composition of OLO employed in this study was $\text{Li}_{1.167}\text{Ni}_{0.233}\text{Co}_{0.1}\text{Mn}_{0.467}\text{Mo}_{0.033}\text{O}_2$. Cathodes were made of 94 wt.% electrochemically active material (a mixture of 30 wt.% OLO and 70 wt.% LiCoO_2), 3 wt.% conductive carbon black (Super P), and 3 wt.% polyvinylidene fluoride (PVDF) binder. A separate cathode made of only LiCoO_2 without OLO was prepared as a control sample. The density of active mass layer was controlled at 3.7 g cm^{-3} for all the cathodes regardless of the composition. Jelly rolls comprising the cathodes above, graphite anodes, and polyethylene separators as well as the internal pressure measurement units [20] were provided by Samsung SDI.

Cylindrical cell was fabricated with a jelly roll surrounded by an also cylindrical Teflon spacer filling the void between jelly roll (dia. 10 mm) and cell wall (dia. 18 mm). The bottom of each cell had a hole connected to a pressure sensor (Valcom, VPRF2-2MP). The base composition of electrolytes was 1.3 M LiPF_6 in a mixture of ethylene carbonate (EC), fluoroethylene carbonate (FEC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC) (1:2:2:5 v/v). In the experiments for evaluating additives, the amount of phosphorus derivatives was set at 5 wt.%. Triphenyl phosphine (TPP), ethyl diphenylphosphinite (EDP), and triethyl phosphite (TEP) were purchased from Aldrich and used without further purification.

The cell internal pressure was monitored and recorded during charging at a current density of 0.22 mA cm^{-2} up to 4.53 V with a battery testing system (TOSCAT-3000). The charging capacities of cylindrical cells were around 1050 mAh. After the completion of electrochemical experiment, the electrolyte samples were extracted by centrifugation and analyzed with nuclear magnetic resonance spectroscopy (Bruker, AVANCE Digital 300, 300 MHz and AVANCE III 600, 600 MHz) and a gas chromatography–mass spectrometry (Hewlett Packard, HP 6890/5973).

Linear sweep voltammetry was carried out using a Solartron 1480 potentiostat with a scan rate of 1 mV s^{-1} to assess the electrochemical stability of each phosphorus derivative. A Pt working electrode, an Ag/AgNO_3 reference electrode, and a Pt grid counter

electrode were employed. The potential of the Ag/AgNO_3 reference electrode was calibrated using the reaction between ferrocene and ferrocenium ion before use. For each electrolyte sample, anodic and cathodic linear sweeps were carried out separately with freshly polished Pt working electrode.

The influence of phosphorus derivatives as electrolyte additives on the long-term cycle life of cells were examined using 2032-type coin full cells made of the electrodes prepared above. The cells were cycled for 300 times between 4.53 V and 2.75 V at 1.6 mA cm^{-2} (0.5C). All the electrochemical tests were conducted at room temperature.

3. Results and discussion

While the density of OLO cathode is usually around 2.9 g cm^{-3} or less, it can be comparable to that of LiCoO_2 , 3.7 g cm^{-3} , if mixed with LiCoO_2 as described in the Experimental section. With this approach, the high capacity benefit of OLO can be effectively utilized without sacrificing the volumetric energy density that is particularly important in portable electronics applications.

Fig. 1 compares the voltage profiles and the variation in internal pressure of cylindrical cells during the first charging process. With only LiCoO_2 used as cathode material, the change of internal pressure is not significant and the small pressure growth might be caused by gas evolution accompanying the electrolyte decomposition. On the other hand, with the mixture of OLO and LiCoO_2 applied, the internal pressure increases dramatically up to 2.85 bar at the late stage of charging process, associated with the O_2 gas evolution from the activation of Li_2MnO_3 phase [9–12]. Considering only about 30% of available volume of cell is occupied with the jelly roll while the remaining part filled with Teflon spacer, this value corresponds to nearly 10 bar in a full 18650 cell, which is enough to activate the ventilation system of commercial cylindrical cells.

The molecular structures of phosphorus derivatives used in this study are drawn in Fig. 2. When included in the electrolyte as additives, all of them are found to be effective in reducing the internal pressure of cell comprising the OLO-based mixture cathode (Fig. 1). The maximum levels of pressure are 1.84, 0.96, and 0.84 bar in the case of TPP, EDP, and TEP, respectively. In other words, the magnitudes of pressure reduction are 1.01 bar (TPP), 1.89 bar (EDP), and 2.01 bar (TEP) compared with the additive free electrolyte. The reason TEP shows the highest effect might be in its low molecular weight. If the weight fraction of each additive is the same, the molar ratio of TPP:EDP:TEP equals 1:1.14:1.58. Accordingly, the molarity of

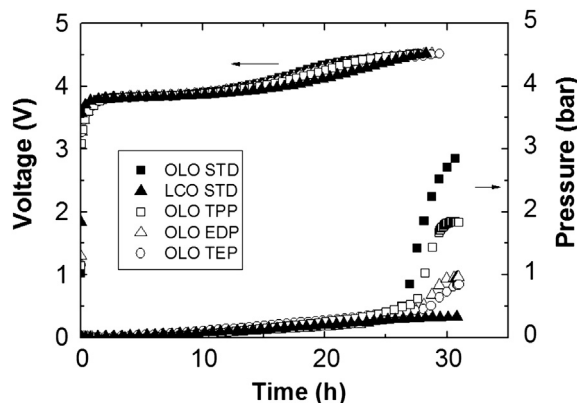


Fig. 1. The voltage profiles and the variations of internal pressure during the first charging of cells containing (■) OLO/ LiCoO_2 cathode and no additives in the electrolyte (▲) LiCoO_2 cathode and no additives in the electrolyte (□) OLO/ LiCoO_2 cathode and 5 wt.% TPP in the electrolyte (△) OLO/ LiCoO_2 cathode and 5 wt.% EDP in the electrolyte, and (○) OLO/ LiCoO_2 cathode and 5 wt.% TEP in the electrolyte.

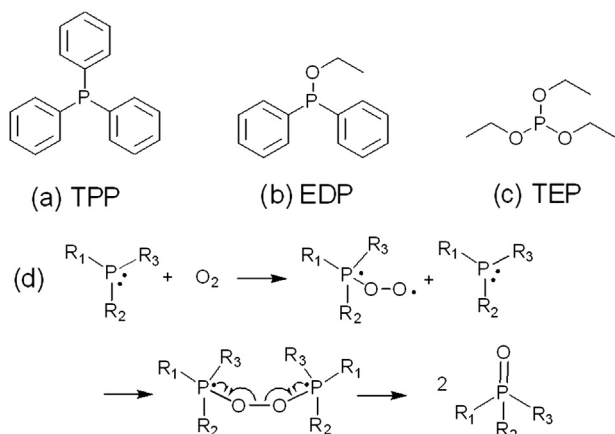


Fig. 2. Molecular structures of (a) triphenylphosphine (TPP), (b) ethyl diphenylphosphinite (EDP), and (c) triethyl phosphite (TEP), as well as (d) a schematic oxidation reaction diagram for those phosphorus derivatives.

TEP is the highest among those additives. In addition to the molarity, the difference of steric hindrance between bulky phenyl group and relatively small ethoxy group can also be considered as an important factor influencing the degree of pressure reduction [21].

While TEP shows the highest magnitude of pressure reduction as anticipated from the molarity and the steric effect, EDP exhibits the highest ratio of pressure reduction to molarity. The values of pressure reduction over molarity are 1.01, 1.66, and 1.27 bar L mol⁻¹ for TPP, EDP, and TEP, respectively, suggesting there might be another factor influencing the effectiveness of additive in absorbing the oxygen. As an effort to clarify this, the electrochemical stability of electrolytes has been investigated using a linear sweep voltammetry technique (Fig. 3). The standard electrolyte (STD), 1.3 M LiPF₆ in EC/FEC/EMC/DEC (1:2:2:5 v/v), exhibits the best stability as expected. Only one peak at 2.5 V corresponding to the reduction of FEC is recognized in the cathodic sweep, and the anodic sweep does not generate a significant current up to 5.5 V vs. Li/Li⁺. The addition of any phosphorus derivative worsens the stability of the electrolyte. The anodic reaction over 4.5 V appears to be specifically severe. The order of anodic stability of additives at around 4.5 V is EDP > TEP > TPP. It is obvious that TEP begins to decompose before 4.5 V and it might be responsible for less effective oxygen absorption ability than anticipated from the molarity and the steric effect.

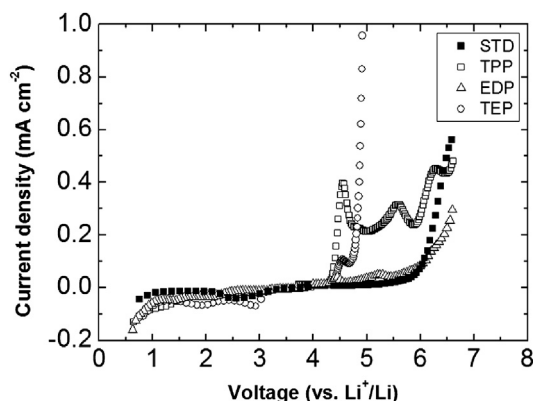


Fig. 3. Linear sweep voltammograms obtained in the electrolytes containing TPP, EDP, and TEP additives respectively in the standard electrolyte (STD) of 1.3 M LiPF₆ in EC/FEC/EMC/DEC (1:2:2:5 v/v). The voltages have been adjusted to be presented vs. Li/Li⁺ in the graph although they were actually measured vs. Ag/AgNO₃.

It is believed that those phosphorus derivatives react with O₂ to form stable compounds that are soluble in the electrolyte as represented in Fig. 2d. The central phosphorus atom of such phosphorus derivatives belongs to the third period in the periodic table, implying that the force between the nuclei and the lone pair electron is relatively weak compared with nitrogen. Consequently, phosphines easily react with O₂ forming phosphine oxide compounds, in which a double bond between the phosphorus and the oxygen atom is present [21,22]. Sulfur compounds can also be regarded as potential additive candidates playing a similar role. However, they generally have low oxidation potential, so can be readily decomposed during cell charging process.

We have characterized the chemical state of additives with ³¹P NMR (Fig. 4) and gas chromatography–mass spectrometry (GC–MS, Fig. 5). Since the ³¹P NMR data after 1 month aging have been taken at 600 MHz instead of 300 MHz, the splits of chemical shift corresponding to the phosphorus nuclei of LiPF₆ are different, but the chemical shifts are the same. Each purchased phosphorus derivative has a small amount of its oxidized form due to the absorption of oxygen in the air. The smaller peak in each ³¹P NMR spectrum of unpurified chemical can be assigned to the chemical shift representing the oxidized form. In the case TPP is used as additive, the change of ³¹P NMR spectrum after the first charging is prototypical. We can assume that TPP (−5.8 ppm, the chemical shift in ³¹P NMR) has reacted to produce triphenyl phosphine oxide (31.2 ppm) [23]. The presence of triphenyl phosphine oxide is also confirmed with GC–MS (compound (2) in Fig. 5) whereas a

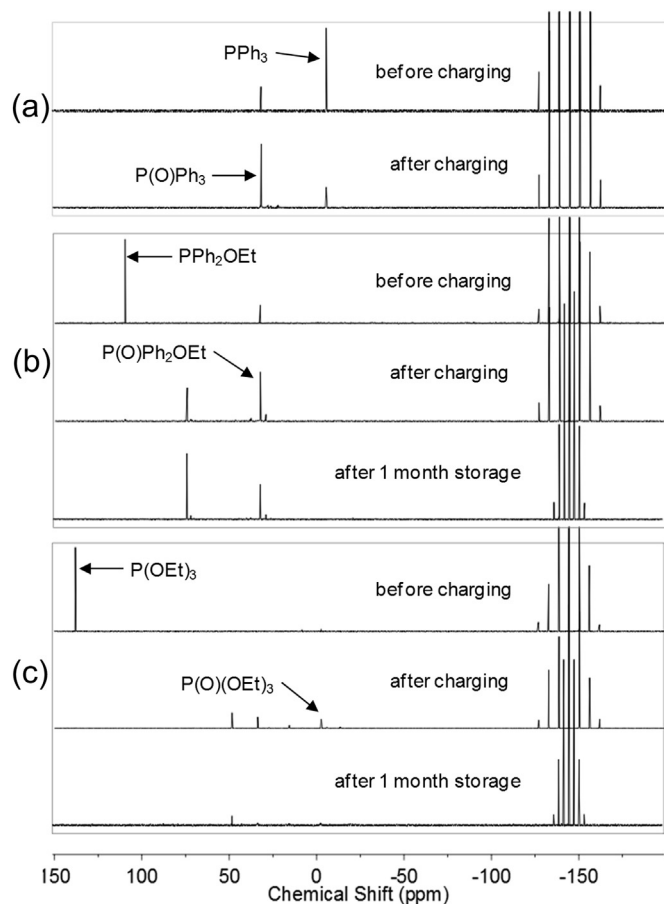


Fig. 4. ³¹P NMR spectra of electrolytes containing (a) 5 wt.% TPP, (b) 5 wt.% EDP, and (c) 5 wt.% TEP before and after the first charging. The NMR spectra were taken at 300 MHz excepting the electrolytes stored for 1 month which were analyzed at 600 MHz.

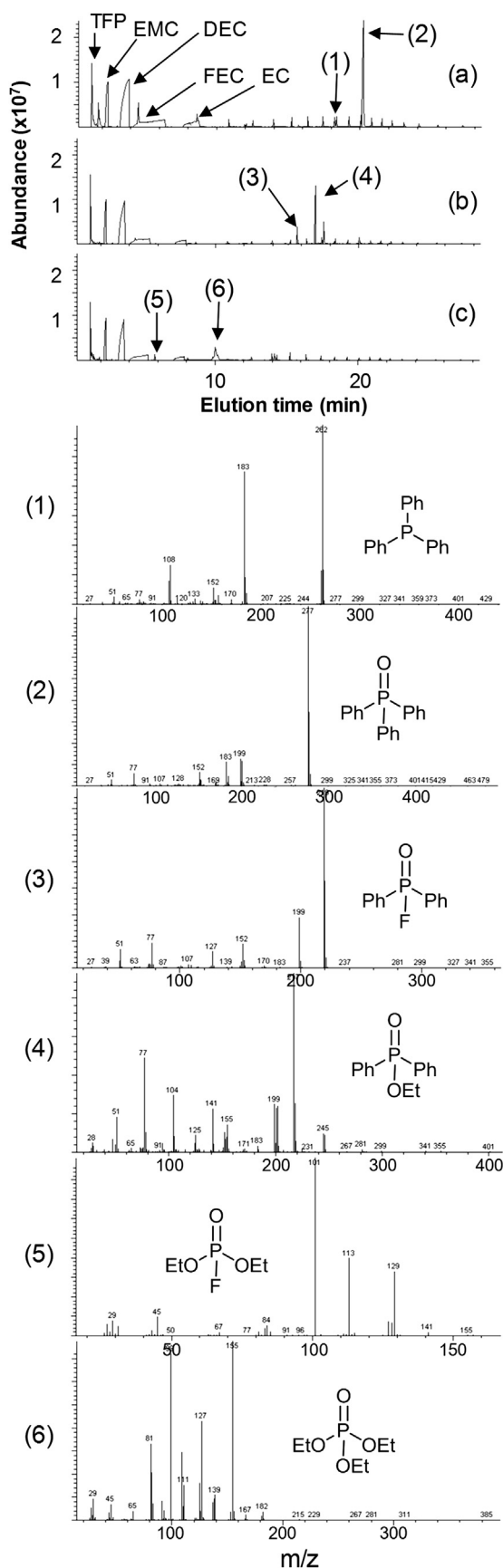


Fig. 5. Gas chromatographic data of the electrolytes containing (a) 5 wt.% TPP, (b) 5 wt.% EDP, and (c) 5 wt.% TEP after the first charging and the mass spectra associated with the peaks denoted as (1)–(6) in the chromatograms.

significant amount of TPP still remains after the first charging. The reactivity of TPP with O₂ appears to be obstructed by three bulky phenyl groups. The case of EDP is more complicated. The peak corresponding to EDP (109.9 ppm) [24] has completely disappeared after the first charging while the characteristic peak corresponding to ethyl diphenylphosphinate (32.5 ppm, detected also in GC–MS, compound (4) in Fig. 5) [25] has emerged. A new peak at 74.4 ppm suggests the formation of another compound that is not detectable in GC–MS due to the thermal decomposition inside the GC column. The extracted electrolyte was stored under Ar atmosphere in a glove box for 1 month and characterized with ³¹P NMR again. Astonishingly, the peak at 74.4 ppm has further grown while the peak corresponding to ethyl diphenylphosphinate has dwindled, indicating the unknown compound is a decomposition product of ethyl diphenylphosphinate in the electrolyte. It is known that alkoxy derivatives of phosphine oxide, such as phosphonite, phosphonate, and phosphate, can be attacked by various nucleophiles or undergo acid-catalyzed reaction to form various decomposed products [26–29]. The case of TEP is more complicated but its behavior is similar to that of EDP. TEP (138.0 ppm) [24] has transformed to triethyl phosphate (−2.7 ppm, detected also in GC–MS, compound (6) in Fig. 5) [24] and a mixture of unknown compounds (48.3, 33.7, and 15.6 ppm, respectively). The peak intensity ratio of the triethyl phosphate to LiPF₆ has also decreased after 1 month storage in an inert atmosphere indicating the further decomposition of triethyl phosphate. Due to the limited amount of electrolyte extracted from the cell, the purification and analysis of each decomposed compound of phosphine additive has not been performed.

More compounds are identified in the GC–MS results. For example, trifluorophosphine oxide (TFP), which is not detected with NMR, is noticed at the elution time of 1 min in the GC–MS data. It is assumed that the thermal decomposition of LiPF₆ is accelerated in the course of gas chromatography measurement. Even some fluorine-substituted phosphine oxide compounds are found: fluoro diphenyl phosphine oxide (3) and diethyl phosphorofluoridate (5) in Fig. 5. They might have been formed from the reaction of fluoride, derived from the decomposition of LiPF₆ in GC, with ethyl diphenylphosphinate and triethyl phosphate, respectively. Smaller peaks, spaced regularly from 10 to 25 min in eluent time, are corresponding to the LiPF₆ decomposition products in GC.

Fig. 6 shows the room-temperature cycling performance of the 2032-type coin cells containing no additive, 5 wt.% TPP, 5 wt.% EDP, and 5 wt.% TEP. The capacity retention values after cycling 300 times are 18 (no additive), 42 (TPP), 45 (EDP), and 56% (TEP), respectively. Obviously, the use of phosphorus derivatives improves

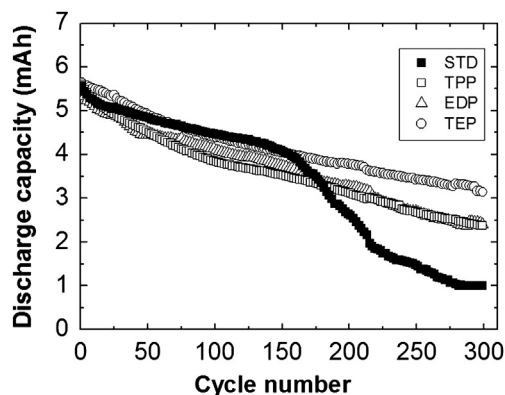


Fig. 6. Cycle life of 2032-type coin cells containing TPP, EDP, and TEP additives in the standard electrolyte (STD).

the cell cycle life significantly. Whilst the reason for much improved performance of cells having additives has to be further explored, it is in accordance with the previous reports on phosphine and phosphine oxide derivatives as electrolyte additives [15–18].

4. Conclusions

In summary, the use of phosphorus derivatives as additives in electrolyte allowed us to considerably mitigate the internal pressure of cylindrical cells containing OLO-based cathode materials at the end of charging process. The oxygen-absorbing reaction of those phosphorus derivatives was confirmed with ^{31}P NMR spectroscopy. In addition, those additives were found to improve the cycling performance of cells.

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